1903

The electrolytic refining of copper

Lewis S. Logan

Frank R. Bell

THESIS

FOR THE

Degree of Bachelor of Science

IN

MINE ENGINEERING.

SUBJECT:

"The Electrolytic Refining of Copper."

LEWIS S. LOGAN AND FRANK R. BELL.

CLASS OF 1903.

ELECTROLYTIC REFINING OF COPPER.

Introduction.

Although copper can be separated from its solution by means of the electric current and the amount so separated varies directly as the current, there is a point in each and every solution where on account of the energy given off to the ions, the copper will be carried over in a more or less impure state, depending upon the strength of the current, the strength of solution, whether it is saturated or only partly saturated, or whether normal basic or acid and also upon the amount of impurities in the solution.

It is the purpose of this thesis

(1) With a neutral solution of $CuSO_4$, varying in strength from a one-fourth saturated to a saturated solution, to find the strength of current at which the oxide of copper will be deposited on the cathode.

(2) With solution of same strength but varying the amount of H_2SO_4 from 1 to 10 cc, to find the strength of current necessary to deposit copper oxide.

(111) To find the effect of lead, arsenic, antimony, bismuth and tin on the deposited copper.

The impurities were added to the anodes as they were molded. The current was kept constant, at two amperes, and analysis of the refined copper was made at regular intervals of time.

The tests were made first in a normal saturated solution of 700 cc, $CuSO_4$, second, after adding 10 cc H_2SO_4 to the above solution and third, after adding 50 cc more of H_2SO_4. The solution was kept up to the referred volumne by the addition of normal saturated solution of $CuSO_4$ as the old solution evaporated.

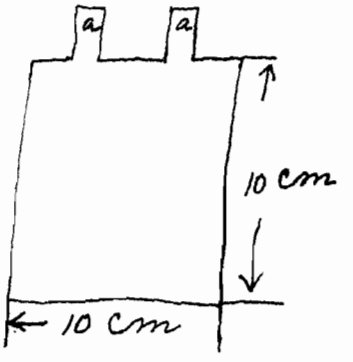
Apparatus.

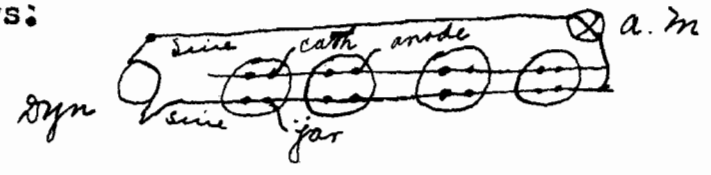
The following is a list of the apparatus used and description of the more important.

1 Dynamo
2 Electrodes
3 Electrolyte
4 Battery Jars
5 Frame to support Electrodes
6 Voltmeter, Ammeter and Rheostat.
7 Chemicals and Laboratory apparatus for making determinations.

(2) The dynamo used was of the Westinghouse type of 110 volts, the proper current being obtained by a Rheostat. A part of the time, at night, the town circuit was used. It being 220 volt circuit, lights and rheostat were used for resistance.

(2) The electrodes used in No's 1 and 11 being eight in number, four anodes and four cathodes were made from sheet copper and of form and size shown. The arms a,a being bent so as to hang on the copper wires used as conductors. The four jars were placed in series. The top of the jars were used as supports for the electrodes and were connected as follows:





The electrodes used in No 111 consisted of eight cathodes and sixteen anodes. The cathodes were same as used in No's 1 and 11. The anodes were made of same area but had a thickness of about 1 c.m. The anodes were molded by taking pure granulated copper, placed in an assay crucible and melted in small Fletcher furnace. After the copper was well fused two and one-half percent of the impurity was added and then the contents of crucible poured into mold. The molds were made by taking equal amounts of fire clay and sand mixed with enough molasses to make plastic and pressed to proper form around a wooden model. The molds were then dried in the muffle of an assay furnace and after being brought to a red heat the molten copper was poured into them. Should there be any moisture left in the molds it would cause the molten copper to spurt and leave blow holes in the anode. The anodes weighed 200 grams each.

Only two anodes had the same impurity or impurities in them. If two

impurities were fused into the same anode there was two and one-half per cent of each impurity used. The impurities used were as follows: No.1 Pb, No11, Pn & Sn, No 111 As, No1V, As & Sn, No V Sb, NoVL Sb & Sn, No V11, Bi, NoV111, Bi & Sn.

The jars were placed in series.

Each cathode was placed between two anodes so that the copper was deposited on both faces of the cathode but taken from only one face of the anode. The electrodes were hung from copper wire conductors, fastened to a wooden frame coated with paraphin to prevent a short circuit. The wires also had small rubber coverings to prevent them from coming in contact with staples which held them in place on frame. Two anodes of same impurities were hung on one wire so that current would go from them through electrolyte to both faces of cathode and then conducted by wire to the next two anodes, etc. The plan of connection being as follows:

3) The electrolyte was prepared by dissolving 35'0 gr of $CuSO_4$ to the litre of water, afterwards adding the required amount of acid. The water was not distilled but taken from hydrant.

(4) The jars were ordinary cylindrical battery jars 4 1/2 " in diameter and 6 " deep.

(4) The frame being rectangular in form was 40" long and 6" wide, was made of wood and held up even with top of battery jars by four small woodenlegs.

(6) The voltmeter and ameter were of the Weston type. The voltmeter, reading to fifty volts and graduated to read one volt. The ameter was a Milli voltmeter with a three amp shunt, reading to three amp and graduated to read .2 amp.

(7) The determination for the impurities were made by determining the percentage of the impurities and taking the rest as pure copper. The determinations were made as follows:

Lead.

Dissolve from five to ten grams in nitric acid (two parts concentrated acid and one part water) taking care to use no more acid than necessary. When solution is effectually heated to expell red fumes and excess of acid, dilute to 300 cc with water, add 2 cc of concentrated sulphuric acid, stir and allow to stand over night. Filter off the precipitated lead sulphate and wash with a one percent solution of sulphuric acid until free from copper salts. Now add to the sulphate of lead remaining on the filter hot ammonium acetate and allow it to run through into a clean beaker. Accidify the solution in the beaker with acetic acid, dilute to 250 cc with hot water, and heat to boiling. Run in from burette the standardize solution of ammonium molybdate until all the lead is precipitated, stirring thoroughly after each addition of the molybdate and testing a drop of the solution from time to time on a porcelain plate with tannin solution. From number of cc of molybdate solution used calculate the percent of lead.

Arsenic.

Disolve five to ten grams of nitric acid,heat to expell red fumes, add a small crystal (one gram) ferric ammonium sulphate,stir,add an excess of ammonia. Heat to boiling,and filter off the precipitated ferric hydrate,which will contain all the arsenic. Wash with dilute ammonia water,dry and ignite the precipitate. The ignited precipitate is fused with eight parts of a mixture of pure sodium carbonate and potassium nitrate. Disolve the fused mass in hot water,filter and wash with hot water. The arsenic is now in solution. Acidify with nitric acid and add a drop or two in excess. Now add a large excess of zinc oxide and if much of a precipitate is formed filter and add a little more zinc oxide. A neutral solution of silver nitrate is now added in slight excess and allowed to stand until the precipitation of the brick red silver arsenic is complete. Filter and wash with cold water until free from silver. Disolve the precipitate through the filter with dilute nitric acid into beakers,add a few cc of ferric alum,and titrate with standard solution of ammonium sulphocyanide.

Antimony.

Disolve five to ten grams in nitric acid,heat to expell red fumes, dilute to about 300 cc and add a small crystal of ferric alum.

Render the solution ammoniacal,heat to boiling,add one gram ammonium carbonate and a little sodium phosphate. The precipitation of antimony is complete. Filter off the precipitate,wash with water,containing a little ammonia and disolve in a little dilute hydrochloric acid.

Dilute the solution and pass into it sulphurated hydrogen. Add 10cc of yellow ammonium sulphide and warm gently for one hour. Filter and wash. The filtrate will contain the antimony which is precipitated by the addition of a little hydrochloric acid. Filter,wash and disolve the antimony sulphide with a little concentrated hydrochloric acid. Dilute the filtrate,pass sulphmetled hydrogen,filter and wash with hot water. Wash finally with alcohol to displace the water and when dry wash with carbon disulphide to disolve the free sulphur and dry at a temperature not over 100 degrees C. When dry place filter and precipitate into a weighed crucible and moisten with 2 to 4 cc of nitric acid and evaporate to dryness on water bath. Finally ignite cautiously over Bunsen burner and weigh as antimony tetroxide. SB_2O_4

Bismuth

Disolve five to ten grams in nitric acid,dilute to 200 cc,add ammonia in excess and a slight excess of ammonium carbonate solution,boil fifteen minutes and allow to stand until the bismuth carbonate settles,filter,wash, weight as Br_2O_3.

Tin.

Disolve five to ten grams in nitric acid,dilute to 300 cc and boil to ensure complete precipitation of the hydrated oxide of tin. Filter, wash,ignite and weigh as SnO_4.

Experiment 1.

With a normal solution of copper sulphate,having the strength of 1/8,1/4,1/2 and fully saturated solution to find the strength of current, at which the oxide of copper will be deposited on the cathode.

m As long as pure copper was being deposited there would be no bubbling at the cathode,but as soon as the oxide would begin to be deposited,small bubbles would form,first on the face of the cathode then rise to surface of solution.

The oxide would always form first on the edges of cathode and in time its entire face would be covered.

Then would be up to a certain strength of current where pure copper would be deposited,then an increase of current,a deposit of copper and copper oxide and finally the entire deposit would be copper oxide. The table shows the greatest current of pure copper and current at which entire deposit was copper oxide.

Table.

Solution	Cur. for pure Cu		Cur. for CnO	
	Amp.	Volt	Amp	Volts.
1/8 Sat	.3	1	.6	2
1/4 "	1.5	2	4.	6
1/2 "	6.	7	10	11
"	8.	6.5	14	12.

Experiment 11.

With solutions of same strength but varying the amount of sulphuric acid from one to ten cc,find the strength of current necessary to deposit copper oxide.

Only the saturated and 1/8 saturated solutions were tested. The others ranging between these according to strength of solution. The voltage given in that taken for a constant current one ampere.

Amt. H_2SO_4	1/8 Sat. Solution Amp	Volt	Saturated Solution. Amp.	Volts
1	8.	7	1.5	2.5
2	1.	7	1.8	2.5
4	1.2	6	2.2	2.
6	1.3	5 1/2	2.5	1.5
8	1.4	4 1/2	2.8	1.
10	1.8	4	3.4	.5

Experiment 111

To find the effect of lead, arsenic, antimony, bismuth and tin on the deposited copper keeping current constant.

First, In a normal saturated solution of copper sulphate.

The determinations were made each time after a run of eight hours. The cathodes were slightly coated with vaseline to facilitate the removal of deposited copper.

The general effect of the impurities in the deposited copper when they did begin to show were as follows:

Tin seemed to counteract the bad effect of each impurity, used with it.

Lead in general gave the deposited copper a dark color, made it rough and with the highest percentage obtained quite brittle.

Arsenic seemed to have but little effect and when it was found the

deposited copper had a slight golden color but quite tough and evenly deposited.

Antimony when with tin had but little effect on either the toughness, color or smoothness of deposit. However when it was the only impurity it gave to the deposited copper many rainbow colors, made it quite brittle and the deposit would be in ridges running vertically on the cathode.

Bismuth.

Bismuth seemed to have the most detrimental effect of all, making the copper very brittle and often copper oxide was deposited on the cathode, while others had no oxide at all deposited. Also deposit was quite crystalline and had many little blisters over the face of the cathode. The deposit with bismuth and tin had a slick greasy appearance and was just as brittle as that with bismuth alone.

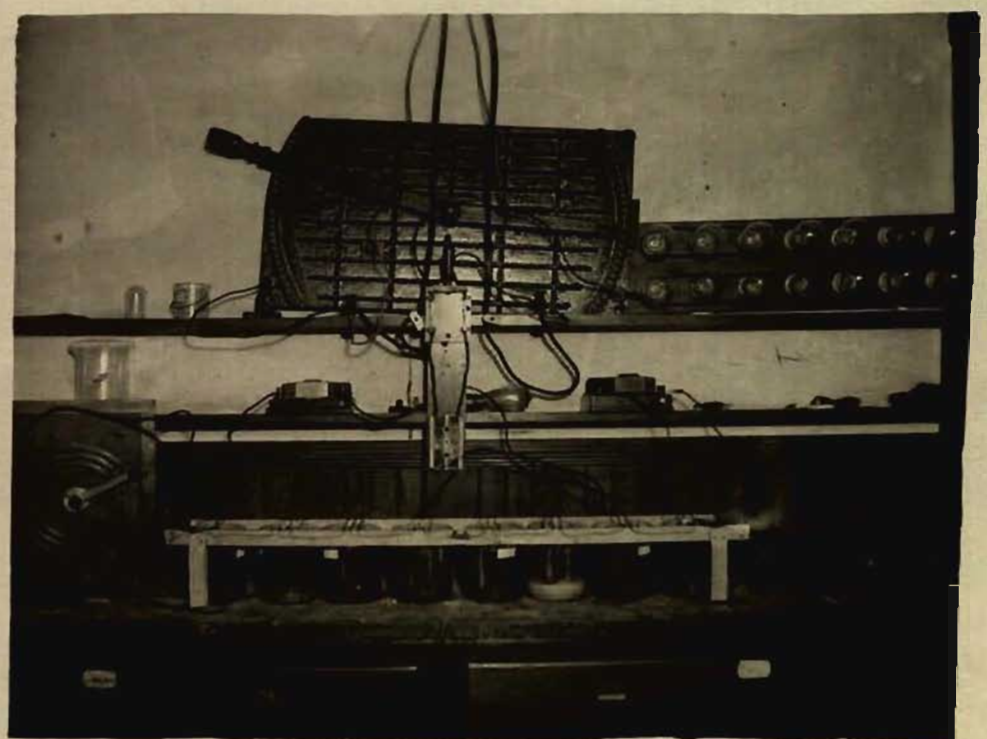
Second. To find the effect when ten cc of soluphric acid was added to solution.

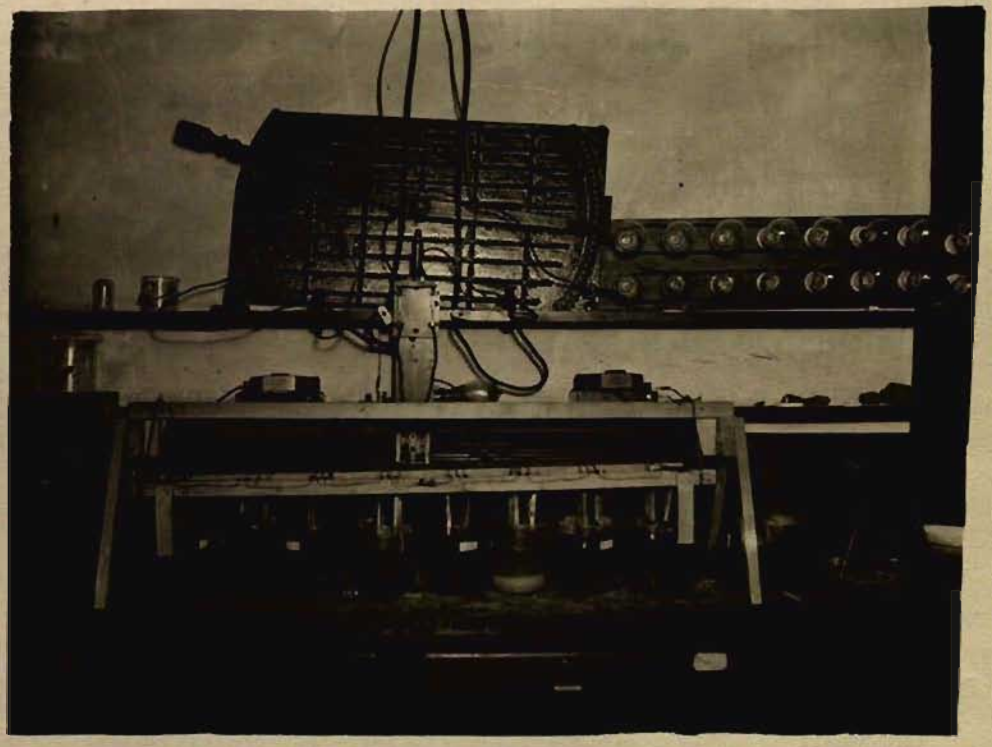
The results obtained seem to show that all the acid was used up as soon as added. Thus take No's 1 and 11. The amount of lead in No 1 is less than that in No11, where in previous runs it was the reverse, showing that all the acid was used up in disolving lead in No1 while in No 11 both lead and tin were dissolved.

Third. The affect after adding 50 cc more of acid to the solution.

The following is a tabulation of the amounts of the impurities found after each run.

A determination of the impurities in No's 1 to 5 was made every eight hours and in No's six to nine every ten hours. Constant current of 2 amp





was used throughout.

A normal saturated solution was used in No 1-5,10 cc sulphuric acid added in No's 6-8,50 cc more sulphuric acid added in No's 8 and 9.

The weight of copper deposited in No's 1 and 6-9 was found by first weighing the cathode and then weighing cathode and deposited copper and taking the difference. Also the amount of copper deposited per ampere was determined.

	Run NO I		Run No 6		Run No.7.	
No.of cath.	gr cu	gr per amp hr	gr cu	gr 1 amp hr	gr cu	gr 1 amp hr.
I	18.4	1.1525	40.8	1.275	35.5	1.1094
II	18.3	1.15189	40.5	1.2656	36.5	1.1406
III	18.3	1.15189	40.4	1.2621	36.	1.135
IV	18.3	1.15189	35.	1.2188	36.	1.135
V	18.8	1.155	41.	1.2885	33.5	1.05
VI	18.6	1.15475	40.5	1.2656	36.	1.135
VII	11.1	.69475	31.5	.9844	32.6	1.0188
VIII	12.2	.7625	40.1	1.2225	36.5	1.1406

	Run No.8		Run No.9	
No Cath.	gr cu	gr per amp hr.	Gr cu	gr one amp hr.
I	38.5	1.2031	38	1. 1872
II	38.5	1.203[illegible]	38	1.1872
III	38.	1.1872	38.5	1.2031
IV	38.5	1.2031	37.5	1.1718
V	37.5	1.1718	37	1.1506
VI	38.5	1.2031	38.5	1.2031
VII	35.	1.0906	37.5	1.1718
VII	38.5	1.2031	36.5	1.1406

Pb.

No of run	Amt.Taken	Amt obtained	Percent Pb	Percent Cu.
1	8.051	none	.00	100.
2	8.869	.0178	.139	99.861
3	6.82	.01336	.186	99.814
4	7.547	.019	.265	99.735
5	7.469	.026	.348	99.652
6	7.742	.00967	.012	99.988
7	7.554	.0261	.345	99.655
8	7.523	.0126	.167	99.833
9	7.826	.025	.320	99.68

Pb and Sn.

No.run.	amount taken		Amount obtained		%Pb	% Sn	% Cu.
	Pb	Sn.	Pb	Sn			
1	7.024	7.46	none	none	0.0	0.0	100.
2	6.6159	5.631	.00522	.00952	.019	.015	99.916
3	7.852	7.244	.0077	.0112	.098	.153	99.749
4	7.643	7.942	.0146	.0162	.191	.204	99.605
5	8.557	8.263	.01964	.01888	.229	.228	99.543
6	7.213	7.592	.01152	.0072	.16	.094	99.746
7	7.652	7.299	.0135	.0145	.117	.198	99.685
8	7.428	7.731	.0116	.00024	.156	.031	99.814
9	7.592	7.047	.017	.012	.224	.169	99.607

As

NO.of run	Amount taken	Amount obtained	Percent As.	Percent Cu.
1	15.583	none	0.0	100.
2	7.0155	none	0.0	100.
3	7.131	.0054	.076	99.924
4	7.524	.0097	.013	99.87
5	8.1414	.0142	.174	99.826
6, 7	no arsenic was found			
8, 9	no arsenic was found.			

As and Sn.

No.run	amount taken		Amount obtained		% As	% Sn	% Cu.
	As	Sn	As	Sn.			
1	5.378	5.462		none	0.0	0.0	100.
2	6.315	6.461	none	.0132	0 .0	.02	99.98
3	7.058	7.477	.0047	.0168	.076	.222	99.702
4	7.543	7.645	.00685	.0194	.091	.254	99.655
5	8.526	7.469	.00874	.02607	.102	.348	99.55
6, 7	No As found						
8, 9	No As found.						

Sb.

No. run	Amount taken	Amount Obtained	Percent Sb	Percent Cu.
1	8.051	none	0.0	100.
2	8.869	.0178	.139	99.861
3	6.82	.01336	.186	99.814
4	7.547	.019	.265	99.735
5	7.469	.026	.348	99.652
6	7.803	.0076	.096	99.904
7	7.733	.0114	.187	99.813
8	7.298	.0135	.185	99.815
9	7.851	.0248	.316	99.684

Sb and Sn.

No. run	Amount taken		Amount obtained		% Sb	% Sn	% Cu.
1	8.651	7.137	none	.012	0.0	.15	99.85
2	5.52	7.673	.0064	.0164	.118	.21	99.672
3	7.052	5.604	.01124	.01135	.219	.203	99.578
4	7.531	7.465	.0163	.0198	.217	.252	99.531
5	7.952	7.576	.02353	.025	.315	.31	99.375
6	7.951	7.814	none	.00112	.0	.014	99.986
7	8.41	7.192	.00816	.0063	.097	.089	99.814
8	7.384	7.238	.0027	.008	.036	.0114	99.85
9	7.787	7.599	.0064	.027	.082	.359	99.559

Bi.

No.run	Amount taken	amount obtained	percent Bi	PercentCu.
1	5.3845	.0018	.035	99.967
2	5.4205	.00945	.174	99.826
3	10.1	.03006	.298	99.702
4	8.245	02475	.301	99.649
5	8.022	.02826	.353	99.647
6	7.5415	.0315	.428	99.58
7	7.3025	.0365	.548	99.452
8	7.525	.031	.408	99.592
9	7.151	.032	.461	99.539

Bi and Sn.

No. run	Amount taken		Amount obtained				
	Bi.	Sn.	Bi	Sn.	% Bi.	% Sn	% Cu.
1	5.327	5.1315	.00162	.0114	.0306	.171	99.967
2	4.5835	7.027	.0027	.0163	.059	.131	99.826
3	10.428	10.485	.0267	.0185	.256	.176	99.702
4	7.518	7.357	.01668	.01357	.261	.184	99.699
5	7.319	7.085	.02016	.0134	.275	.189	99.647
6	7.741	7.531	.046	.0035	.597	.037	99.366
7	7.561	7.389	.1062	.0102	1.448	.146	98.306
8	7.694	7.525	.058	.029	.774	.385	98.831
9	7.088	7.214	.065	.028	.915	.403	98.682